

## Concentration Determinations for Reactive Chemical Intermediates Using Empirically Determined and Theoretically Calculated Transition Probabilities

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The Beer-Lambert law, after invoking several usually applicable approximations, shows that the fractional absorption of radiation on a transition between two quantum states is proportional to the concentration of molecules present in the lower state. For non-reactive molecules, a suitable standard of known concentration/pressure can be used to determine the proportionality constant, i.e., the product of the path length and molecular cross section. However, for many chemical intermediates such as free radicals, their reactivity precludes preparing such a standard of known concentration and accounts for the frequent absence of their cross sections in molecular line lists. Nonetheless, such molecules play important roles in chemical reactions of significance both economically and environmentally; hence spectroscopic measurements of their concentrations can be very valuable. The peroxy radicals, RO<sub>2</sub> (R=H or alkyl group), are important intermediates in combustion and tropospheric chemistry and experimental cross-sections have been reported for several peroxy radicals using indirect means to determine their concentrations. However, today it is also possible to calculate cross sections for individual rovibronic transitions using a combination of quantum chemistry methods and spectral simulation software. In our work the CFOUR quantum chemistry suite and the PGOPHER spectral simulation software were used. The purpose of this poster is to describe our computational approach and compare its results with experimentally determined values.

To determine cross sections, one needs to calculate the vibronic transition dipole moment (VTDM)

$$M_{vibr} = G_{v''v'} M_e^{AX}$$

where  $G_{v''v'}$  is the Frank-Condon (FC) overlap integral, and  $M_e^{AX} = \langle \tilde{A} | \mu | \tilde{X} \rangle$  is the electronic transition dipole moment (ETDM) for the experimentally observed  $\tilde{A} \leftarrow \tilde{X}$  electronic transition of the peroxy radicals. To calculate the FC overlap integral, geometry optimization and normal mode analysis were performed for the ground and excited states using the UHF-CCSD(T)/ANO1 method. The FC overlap integral was obtained as the square root of the FC factor calculated with the “FC-squared” ([FC]<sup>2</sup>) program available in CFOUR. The ETDM values for the  $\tilde{A} \leftarrow \tilde{X}$  transition were calculated at both the  $\tilde{X}$  and  $\tilde{A}$  state optimized geometries using the UHF-EOMEE-CCSD/aug-pVTZ method. Averaging these ETDM values accounts for its linear dependence on geometry configuration. Based on extensive calculations for HO<sub>2</sub>, a scaling factor of 0.95 was adopted for all RO<sub>2</sub> radicals to account for higher-level electron correlation and basis set error effects on the ETDM. The calculated values of the VTDM show good agreement with the corresponding values obtained from experiment.